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Merapi Volcano, Central Java, Indonesia:

A case study of radionuclide behavior in volcanic gases and its implications for magma dynamics at andesitic volcanoes

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[1] For more than 20 years, volcanic gases have been regularly collected at Merapi Volcano, Indonesia, and have been subsequently analyzed for their (^{210}Pb), (^{210}Bi), and (^{210}Po) activities and SO_2 contents. These new results show the high volatility of the three radionuclides in andesitic gases, although their emanation coefficients (0.94%, 3.5%, and $\leq 53\%$ for ^{210}Pb , ^{210}Bi , and ^{210}Po , respectively) are significantly lower than those observed at basaltic volcanoes. This emphasizes the major role of magma temperature on the degassing of these metals, which are mainly transported in volcanic gases as Pb-chloride compounds and as Bi- and Po-metallic species. Radioactive disequilibria between ^{210}Pb , ^{210}Bi , and ^{210}Po in the gas phase are characteristic of degassing processes and gas paths within the edifice. Gases released at both Gendol and Woro fumarolic fields are of magmatic origin, but their radionuclide content is strongly altered by secondary processes (chemical reactions with surrounding brines and deposition of sublimates in the ground). High-temperature gases collected in the summit gas plume are of pure primary magmatic origin and are likely directly tapped in the degassing reservoir. Gases arising from the growing domes are strongly depleted in the most volatile isotopes and gas species. This suggests that magma mostly degasses at depth in open system, explaining why the volcano usually undergoes no explosive eruptions. The gas flux at Merapi is sustained by a deep magma supply which is twice the extrusion rate of lava. Unerupted degassed magma thus progressively accumulates beneath the summit, yielding an overpressure which can trigger dome collapse without precursor.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 1040 Geochemistry: Isotopic composition/chemistry; 1065 Geochemistry: Trace elements (3670); 8414 Volcanology: Eruption mechanisms; 9320 Information Related to Geographic Region: Asia; **KEYWORDS:** radioactive disequilibria, volcanic gases, metal volatility, magma degassing, magma dynamics, Merapi Volcano

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1. Introduction

[2] Since the pioneering work of Lambert *et al.* [1976], it is well known that the last decay products of the ^{238}U -series, namely ^{210}Pb , ^{210}Bi , and ^{210}Po in their successive order of decay, are engaged in chemical species that are volatile at magmatic temperatures. Accordingly, these nuclides are strongly enriched in volcanic gases compared to a standard continental atmosphere [Lambert, 1983]. This enrichment is characteristic of each radionuclide: for

instance, ^{210}Po usually is totally expelled from degassing basaltic magmas, whereas ^{210}Bi and ^{210}Pb have emanation coefficients of about 10 to 30%, and of a few percent, respectively [Lambert *et al.*, 1985]. Because of these contrasted volatilities, magma degassing processes strongly fractionate these isotopes, leading to significant radioactive disequilibria in the gas phase. Furthermore, due to their short half-lives (^{210}Pb , $t_{1/2} = 22$ years; ^{210}Bi , $t_{1/2} = 5$ days; ^{210}Po , $t_{1/2} = 138$ days), disequilibria among these radionuclides are potential tracers of events having different timescales, from a few years for the pair ^{210}Po - ^{210}Pb , to a few weeks for the pair ^{210}Bi - ^{210}Pb . Short-lived radioactive

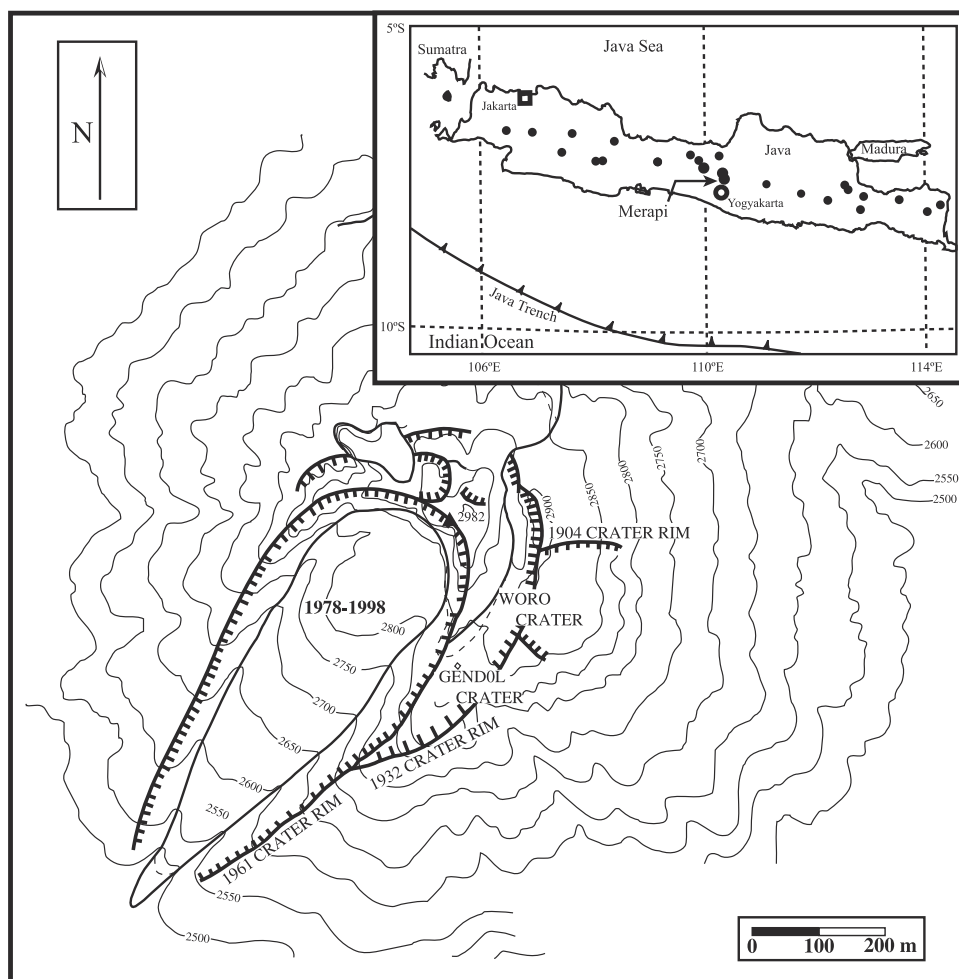


Figure 1. Simplified morphological sketch map of the summit of Merapi Volcano [after Camus *et al.*, 2000]. Contour lines are at every 50 m. The location of Merapi Volcano on Java Island, Indonesia is shown (inset).

disequilibria in gaseous emissions of active volcanoes have been extensively studied over several decades at both Mt. Etna and Stromboli Volcanoes, Italy [e.g., Lambert *et al.*, 1985; Le Cloarec *et al.*, 1988; Gauthier *et al.*, 2000; Le Cloarec and Pennisi, 2001]. At these two open-conduit volcanoes producing mostly undifferentiated, low-viscosity magmas at high temperature (1000–1100°C), the gas phase is released in the atmosphere with little, if any, interaction with solidified host rocks. In such primary magmatic gases, it has been shown that ^{210}Po – ^{210}Bi – ^{210}Pb radioactive disequilibria mostly depend on both the magma residence time within the degassing reservoir and the escape time elapsed between the gas separation from the magma and its emission into the atmosphere, two parameters which are closely related to volcanic activity [Gauthier *et al.*, 2000].

[3] In contrast to these previous studies, we report in this paper the first study of short-lived radioactive disequilibria measured over a long period (1978–1995) in gaseous emissions from Merapi Volcano, a typical andesitic stratovolcano producing magmas with lower temperature (about 900°C) and higher viscosity than Etnean and Strombolian magmas. Merapi Volcano (latitude 7.33°S, longitude 110.27°E, 2947 m

above sea level) is located in Central Java (Indonesia) and belongs to the volcanically active Sunda arc, which is related to the subduction of the Indoaustralian plate beneath the Eurasian plate (Figure 1). It is one of the most active volcanoes among the 128 of the Indonesian arc and is considered as one of the most dangerous. Merapi Volcano has been continuously erupting for the last two centuries, and its eruptive activity is characterized by successive periods of lava dome extrusion, separated by brief destructive events generating pyroclastic flows [Camus *et al.*, 2000; Voight *et al.*, 2000]. Permanent degassing also occurs both through major cracks within the 1961 horseshoe-shape summit crater, and at two high-temperature fumarolic fields located nearby the extrusive dome: Woro ($T = 220$ – 650°C) and Gendol ($T = 600$ – 850°C) (Figure 1). Merapi Volcano is a moderate gas emitter among other arc volcanoes with an average SO_2 flux of about 100 Mg d^{-1} [Nho *et al.*, 1996], reaching 400 Mg d^{-1} during period of intense activity [Symonds *et al.*, 1987]. In this study, we present both radionuclide and SO_2 measurements in gases collected at various places (ancient and growing lava domes within the 1961 crater, as well as fumarolic fields), with the aim to better understand

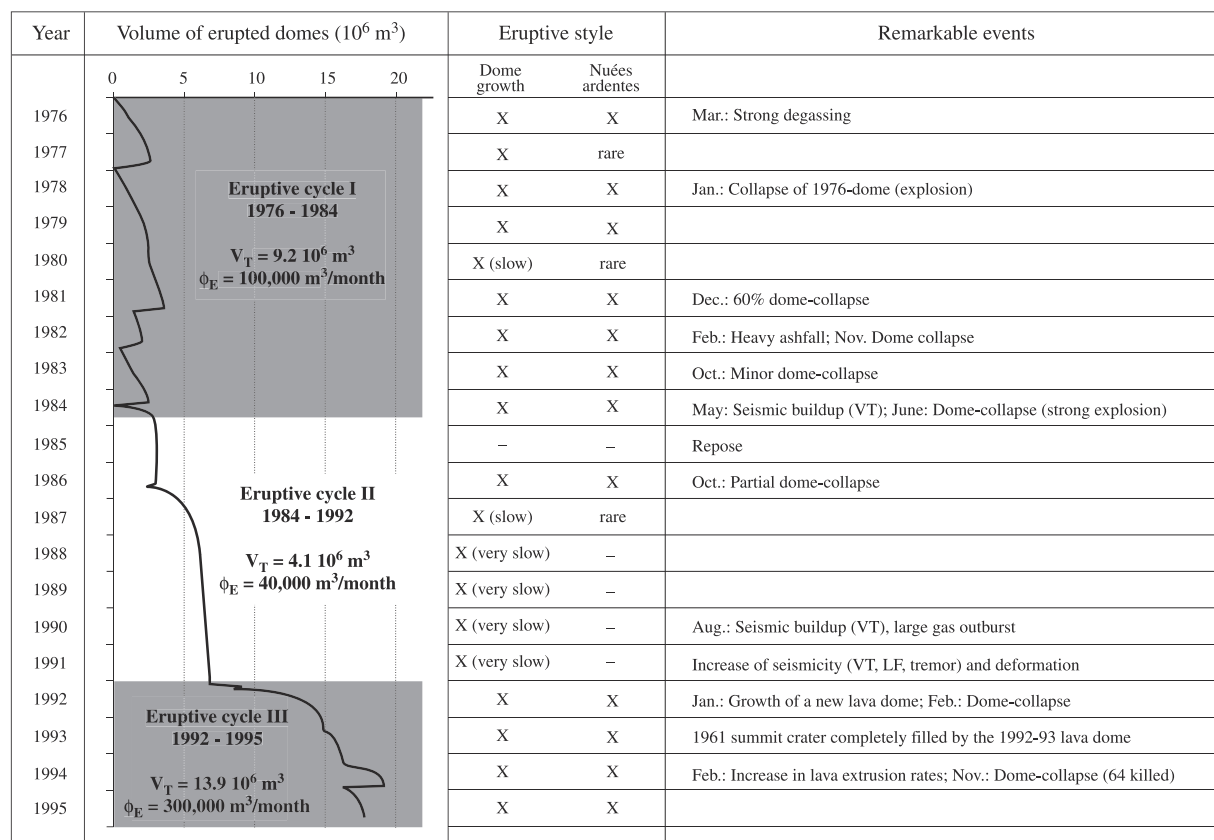


Figure 2. Volume of erupted domes and summary of eruptive activity at Merapi Volcano between 1976 and 1995. Data are from *Siswowidjoyo et al.* [1995], *Kelfoun* [1999], and *Voight et al.* [2000, and references therein]. Average eruption rates (ϕ_E) within an eruptive cycle are obtained by dividing the cumulative volume of erupted lava (V_T) by the duration of the cycle. A cross shows years during which dome growth and/or nuées ardentes occurred; no value shows years during which dome growth and/or nuées ardentes were absent.

degassing processes and to constrain shallow-level magma dynamics at Merapi Volcano.

2. Sampling and Analytical Techniques

[4] From 1978 to 1995, sampling was performed during periods of contrasted volcanic activity. The recent eruptive activity of Merapi Volcano has been extensively studied by different authors and a complete account may be found in the work by *Voight et al.* [2000]. Between 1978 and 1995, three major eruptive cycles can be recognized (1978–1984; 1984–1992; 1992–1995), characterized by mild, low, and high extrusion rates, respectively. Further details on these cycles as well as an overview of the most significant volcanic events having occurred during this period are given in Figure 2. Gas and aerosol sampling was performed at both Woro and Gendol fumarolic fields, and, when allowed by the eruptive activity, in the main plume which is emitted through large fractures opening between the ancient domes and the new growing dome (Figure 1). Under certain circumstances, it was also possible to take samples issued from the growing dome only.

[5] Volatile compounds of ^{210}Pb , ^{210}Bi and ^{210}Po are emitted together with major volatiles at magmatic temperatures, and are subsequently condensed into submicronic

particles when cooled in the atmosphere [*Whitby*, 1978]. Most of the time, these aerosols were collected on blue-type Poelmann-Schneider filters by filtration of several cubic meters of the diluted plume at a flow rate of about 12 m^3 per hour, according to the method described by *Polian and Lambert* [1979]. Additionally, a few samples were obtained at both fumarolic fields through condensation of the gas phase by means of a condenser containing ethylether or chloroform as a cooling agent [*Le Cloarec et al.*, 1994]. Analytical techniques are those described by *Polian and Lambert* [1979]. Activities of ^{210}Bi on filters were measured at the laboratory a few days after sampling with a low-background beta counting unit equipped with a 58 mm-diameter gas flow proportional detector. ^{210}Pb activities were measured with the same apparatus after several months in order to ensure radioactive equilibrium between ^{210}Pb and ^{210}Bi on the filters. ^{210}Po activities were measured on the filters with a low-background alpha counting unit equipped with ZnS scintillation detectors. In condensate solutions, activities of β emitters (^{210}Bi and ^{210}Pb) were measured with a Geiger-Müller counter after spontaneous deposition of ^{210}Bi on a copper disc. Activities of ^{210}Po in these solutions were determined by alpha-spectrometry after spontaneous deposition of this isotope on a silver disc. Further details on these techniques may be found elsewhere

Table 1. The ^{210}Pb , ^{210}Bi , and ^{210}Po Activities (Expressed in Bq m^{-3}) and SO_2 Concentrations (in mg m^{-3}) in Volcanic Gases from Merapi Volcano, 1978–1995^a

Sample Reference	Date	T, °C	(^{210}Pb), Bq m^{-3}	(^{210}Bi), Bq m^{-3}	(^{210}Po), Bq m^{-3}	($^{210}\text{Po}/^{210}\text{Pb}$)	($^{210}\text{Bi}/^{210}\text{Pb}$)	SO_2 , mg m^{-3}	($^{210}\text{Pb}/\text{SO}_2$), Bq g^{-1}	($^{210}\text{Po}/\text{SO}_2$), Bq g^{-1}
<i>Growing Dome</i>										
Dome-8	July 1978	ND	0.88	7.58	0.70	0.79	8.6	ND	ND	ND
Dome-9	July 1978	ND	0.74	6.31	0.33	0.44	8.5	ND	ND	ND
Dome-10	July 1978	ND	1.40	11.6	1.14	0.81	8.3	ND	ND	ND
DMP 7	Oct 1995	ND	0.95	5.10	0.78	0.82	5.4	0.00	ND	ND
DMP 8	Oct 1995	ND	0.34	1.65	0.34	0.99	4.8	0.00	ND	ND
<i>Main Plume</i>										
plume 15	July 1978	ND	0.0238	0.31	0.69	29	13	ND	ND	ND
plume 16	July 1978	ND	0.0111	0.29	0.67	60	26	ND	ND	ND
plume 17	July 1978	ND	0.0111	0.95	0.79	71	85	ND	ND	ND
plume 18	July 1978	ND	0.0111	1.64	0.60	54	148	ND	ND	ND
plume 9	July 1979	ND	0.0076	0.14	0.51	67	18	ND	ND	ND
DMP 2	Sep 1995	ND	0.0088	0.10	0.45	51	11	39.80	0.22	11.3
DMP 3	Sep 1995	ND	0.0186	0.04	1.18	64	2.4	58.39	0.32	20.3
DMP 4	Sep 1995	ND	0.0103	0.25	0.51	49	25	41.01	0.25	12.4
DMP 5	Sep 1995	ND	0.0185	0.14	0.81	44	7.7	38.54	0.48	21.0
DMP 6	Oct 1995	ND	0.0086	0.16	0.53	62	19	24.55	0.35	21.7
<i>Gendol</i>										
Gendol 2A	July 1979	801	0.0877	9.40	11.8	134	107	ND	ND	ND
Gendol 2	July 1979	ND	0.1500	1.72	25.2	168	11	ND	ND	ND
Int. Gendol	July 1979	ND	0.0343	5.56	4.10	120	162	ND	ND	ND
Gendol	Jan 1982	700	0.0135	1.45	2.05	152	107	ND	ND	ND
Gendol	Feb 1988	830	0.0100	2.37	1.37	137	237	24.00	0.42	57.1
Gendol	June 1988	800	0.0275	4.83	5.29	192	176	ND	ND	ND
Gendol 1	July 1988	800	0.0133	0.68	3.88	291	51	ND	ND	ND
Gendol 2	July 1988	800	0.0275	3.11	6.59	239	113	ND	ND	ND
Gendol 1	Sep 1988	800	0.0019	0.16	0.25	129	80	ND	ND	ND
Gendol 2	Sep 1988	800	0.0004	0.03	0.07	168	80	ND	ND	ND
Gendol 3	Sep 1988	800	0.0011	0.12	0.24	216	106	ND	ND	ND
Gendol 1	Aug 1990	ND	0.0417	5.90	2.09	50	142	12.10	3.44	172
Gendol 2	Aug 1990	ND	0.0489	13.6	1.29	26	279	19.00	2.57	68.0
Gendol 3	Aug 1990	ND	0.0444	6.82	2.34	53	154	19.70	2.26	119
Gendol	April 1993	ND	0.0354	6.25	1.35	38	176	66.81	0.53	20.3
GEN 1	Sep 1995	800	0.0410	0.35	4.59	112	8.5	26.86	1.52	171
GEN 2	Oct 1995	660	0.0158	0.11	1.92	121	6.8	44.58	0.36	43.0
GEN 3	Oct 1995	650	0.0096	0.31	0.89	93	32	24.12	0.40	37.0
<i>Woro</i>										
Woro 1	July 1978	ND	0.0301	17.7	1.78	59	588	ND	ND	ND
Woro 1	July 1979	220	0.1042	5.87	43.3	415	56	ND	ND	ND
Woro 2	July 1979	220	0.0729	2.14	35.0	480	29	ND	ND	ND
Woro 3	July 1979	650	0.4722	147	90.2	191	312	ND	ND	ND
Woro 4	July 1979	650	0.3095	108	48.0	155	350	ND	ND	ND
Woro	Jan 1982	ND	0.0123	1.20	0.62	53	97	ND	ND	ND
Woro 1	Feb 1988	572	0.0067	ND	0.20	31	ND	ND	ND	ND
Woro 2	Feb 1988	572	0.0067	ND	0.11	16	ND	ND	ND	ND
Woro 1	July 1994	600	0.0492	1.52	2.37	48	31	28.88	1.70	81.9
Woro 2	July 1994	600	0.0228	0.59	1.00	44	26	20.31	1.12	49.2
Woro 3	July 1994	600	0.0306	1.49	1.65	54	49	24.04	1.27	68.6
Woro	Sep 1995	600	0.0064	0.01	0.54	84	1.9	17.62	0.37	30.7

^aAlso shown are ($^{210}\text{Po}/^{210}\text{Pb}$) and ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios and ($^{210}\text{Pb}/\text{SO}_2$) and ($^{210}\text{Po}/\text{SO}_2$) concentration ratios (in Bq g^{-1}). Radionuclide activities reported in italics are for condensate samples and are given in Bq g^{-1} of water. ND is not determined.

[Le Cloarec et al., 1994]. Activities of the three radionuclides at the time of sampling were then calculated by taking into account their radioactive decay over the course of the analyses. Analytical uncertainties mostly result from the counting statistics and may be estimated at about 5% and 10% (1σ) for alpha and beta countings, respectively.

[6] The sampling device for SO_2 consisted of a filter holder connected to a small pump. The flow rate, calibrated at 2400 m, was about 3 l min^{-1} . Sampling times varied from 10 to 30 minutes depending on the density of the plume. Each filter holder contained two Millipore filters in series impregnated with 1 ml of 1M zinc acetate/10% glycerol solution [Faivre-

Pierret, 1983]. After sampling, SO_2 was eluted from the filters with a solution of 1M zinc acetate/1% glycerol, and subsequently analyzed for sulfite by optic colorimetry using pyridine sodium nitroprussiate as a reacting agent. Analytical uncertainties usually are better than 5% (1σ).

3. Radioactive Disequilibria in Gases: A Tool to Characterize Degassing Processes and Gas Paths in a Volcanic Edifice

[7] Radionuclide activities (in Bq m^{-3}) and SO_2 contents (in mg m^{-3}) in Merapi gases are given in Table 1. Because

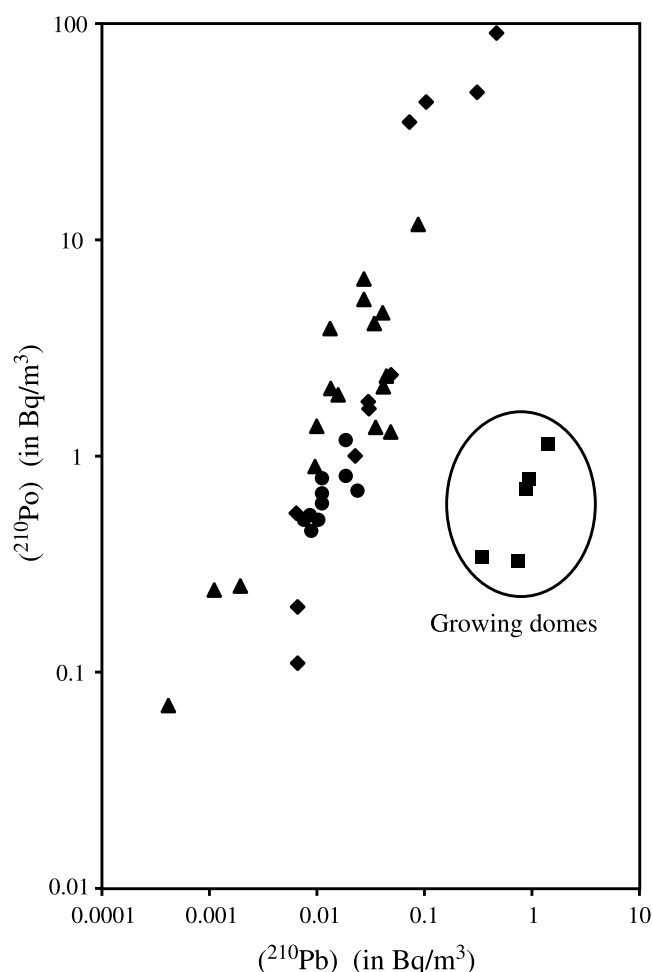


Figure 3. Plot of (^{210}Po) activity versus (^{210}Pb) activity in gas samples collected at Woro (diamonds) and Gendol (triangles) fumarolic fields, in the main plume (circles) and on the growing domes (squares).

observed variations of elemental and isotopic contents in aerosols and gases are mainly due to dilution by air [Lambert *et al.*, 1985; Gauthier *et al.*, 2000]. we also report our data as ratios: ($^{210}\text{Bi}/^{210}\text{Pb}$), ($^{210}\text{Po}/^{210}\text{Pb}$), ($^{210}\text{Pb}/\text{SO}_2$), and ($^{210}\text{Po}/\text{SO}_2$), where parentheses denote activities. The overall correlation between (^{210}Po) and (^{210}Pb) activities clearly indicates a common origin for gases collected at the two fumarolic fields and in the main plume (Figure 3). On the other hand, gases sampled on the growing domes appear to be depleted in ^{210}Po and enriched in ^{210}Pb . The same conclusion applies when considering (^{210}Bi) and (^{210}Pb) activities, although ^{210}Bi is depleted to a lesser extent in fumaroles emanating from the growing dome.

[8] The purpose of the following sections is to describe and explain the isotopic signature of aerosol samples according to their sampling location.

3.1. Growing Dome

[9] The variations of (^{210}Po) versus (^{210}Pb) in gases emitted by the growing dome between 1978 and 1995 are shown in Figure 4. As expected, a linear correlation is observed and corresponds to the dilution of the magmatic plume by air. Its slope gives the best estimate for the

($^{210}\text{Po}/^{210}\text{Pb}$) activity ratio in the gas phase, that is 0.77 ± 0.06 ($R^2 = 0.84$). Note that the same kind of graph could be drawn between (^{210}Bi) and (^{210}Pb), yielding a mean ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratio of 7.66 ± 0.66 ($R^2 = 0.86$). Averaged activity ratios are undistinguishable in 1978 and 1995 samples, which suggests that the composition of the gas phase released from the growing dome remained mostly constant throughout the study period. These ratios, especially ($^{210}\text{Po}/^{210}\text{Pb}$), are unusually low, the lowest ($^{210}\text{Po}/^{210}\text{Pb}$) ratio ever measured being about 4, at Mt. Etna's eruptive vents [Le Cloarec and Pennisi, 2001].

[10] SO_2 measurements performed on the growing dome at the same time (Table 1) show that these gases are also strongly depleted in SO_2 , emphasizing the fact that the magma had already almost completely degassed prior to its extrusion. This is consistent with geochemical and petrographic studies based on feldspar microlite compositions that suggest that lava domes are essentially degassed at the time of their emplacement [Hammer *et al.*, 2000]. This is also consistent with field observations since only a few weak fumaroles can be seen on the growing dome, while the main degassing takes place through major fissures within the 1961 crater (see below). Degassing activity on the growing dome can thus be considered as a residual degass-

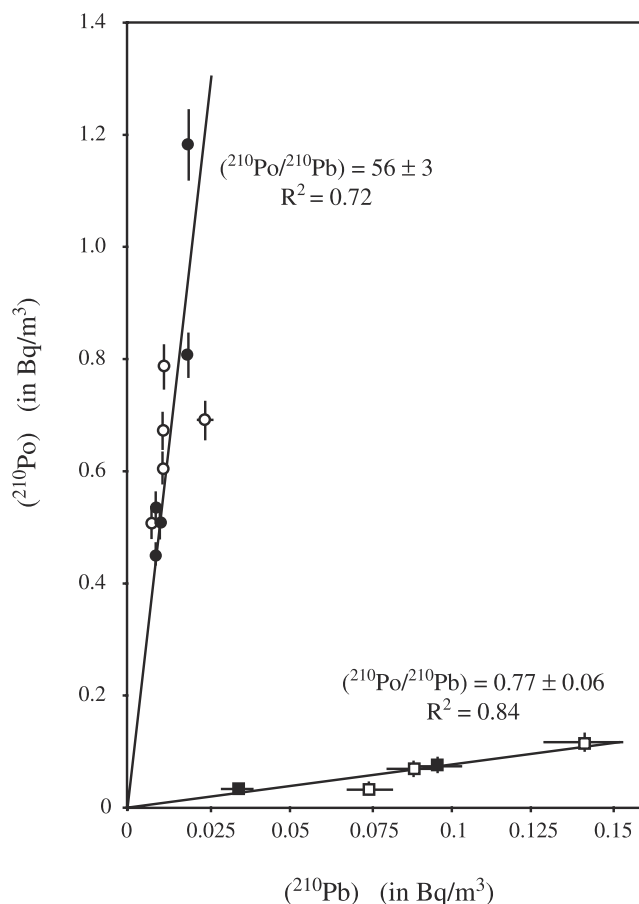


Figure 4. Plot of (^{210}Po) activity versus (^{210}Pb) activity in gas samples collected in 1978–1979 (open symbols) and 1995 (solid symbols), in the main plume (circles) and on the growing domes (squares) (activities scaled down by 10). Error bars (1σ) are based on counting statistics.

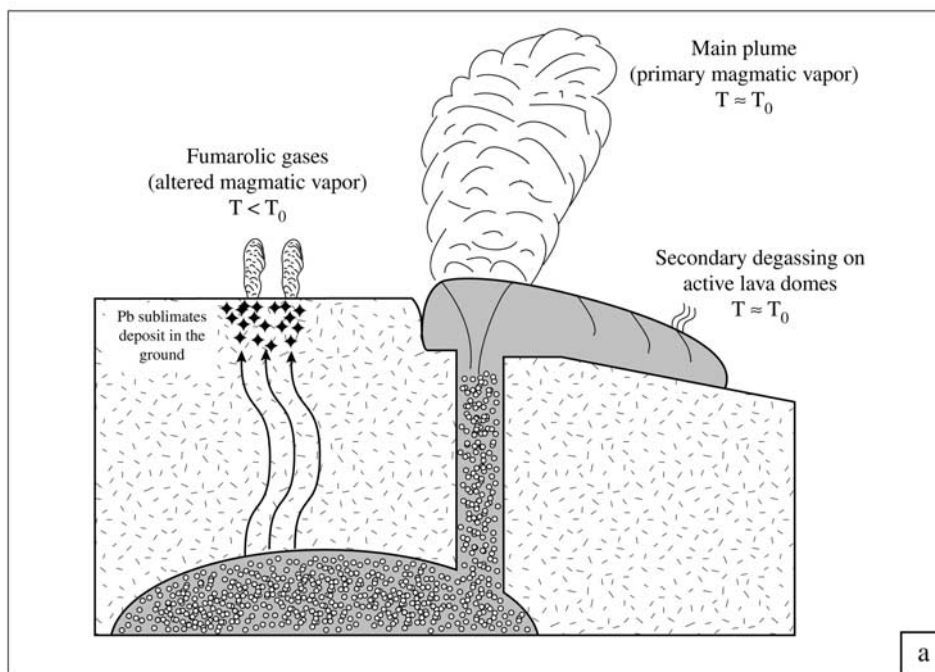


Figure 5a. Schematic representation of a degassing magma system illustrating the three main sources of gas. Primary magmatic vapor is released by the pristine degassing magma, then feeds the main plume with little interaction with host rocks. It also feeds fumarolic fields where both temperature variations within the ground and chemical reaction with host rocks strongly modify its composition due to deposition and/or remobilization of sublimates. As the previously degassed lava cools at the surface, syn-eruptive microlite crystallization may cause concentration of residual volatiles in the molten magma and their subsequent secondary degassing.

ing that might be linked to syn-eruptive crystallization of groundmass phases, which induces concentration of volatiles in the molten magma and their subsequent exsolution [Hammer *et al.*, 2000].

[11] Geochemistry of gases sampled on the growing dome can thus be accounted for by fractional degassing processes, during which the most volatile gases (that is, S-species) and trace elements (like Po, and to a lesser extent Bi) are quickly and thoroughly extracted in the gas phase, thus becoming strongly depleted in the degassed liquid magma [Le Cloarec *et al.*, 1984; Gauthier and Le Cloarec, 1998]. On the contrary, due to its lower volatility, ^{210}Pb is still present in the degassed magma that forms the active lava dome. It is thus continuously emitted as far as the temperature is high enough, provided degassing of major gas species is strong enough to flush trace elements out of the magma. Moreover, the radioactive decay of ^{210}Pb produces a new flux of ^{210}Bi atoms that are subsequently extracted in the gas phase. Radioactive ingrowth of ^{210}Po from its parent, ^{210}Bi , is thus poorly sustained in the degassed magma. This explains why the $(^{210}\text{Bi}/^{210}\text{Pb})$ ratio is higher than the $(^{210}\text{Po}/^{210}\text{Pb})$ ratio in spite of the lower volatility of ^{210}Bi compared to that of ^{210}Po .

3.2. Main Plume

[12] As mentioned above, the main degassing plume is emitted through large fractures between the old domes and the active growing dome within the 1961 crater (Figure 1). Contrary to samples collected on the growing dome,

samples taken in the main plume generally exhibit higher $(^{210}\text{Po}/^{210}\text{Pb})$ activity ratios than $(^{210}\text{Bi}/^{210}\text{Pb})$ activity ratios. This suggests that the magnitude of the disequilibria among these radionuclides is directly constrained by their respective volatility, as one should expect for gases of primary magmatic origin [Gauthier *et al.*, 2000; Le Cloarec and Pennisi, 2001]. With a mean value of about 56 ± 3 ($R^2 = 0.72$), $(^{210}\text{Po}/^{210}\text{Pb})$ activity ratios do not show a large variability over the whole period of sampling (Figure 4). On the other hand, $(^{210}\text{Bi}/^{210}\text{Pb})$ activity ratios present a larger dispersion, ranging from 2 to 150 with a cluster at about 17 ± 6 .

[13] The possible sources of radionuclides, notably ^{210}Bi and ^{210}Po , in a volcanic structure have been discussed elsewhere [Le Cloarec *et al.*, 1994], suggesting that sublimates are an effective source for these radionuclides (Figure 5a). Indeed, when gases are not emitted directly from the magma to the atmosphere, their composition may be depleted or enriched in trace elements by sublimation deposition or mobilization, according to the variations of temperature occurring in the ground, at distance of the magmatic body [Le Cloarec *et al.*, 1994]. Lead compounds, as they are less volatile than Bi and Po ones, are particularly sensitive to temperature fluctuations, and large amounts of lead salts have been observed in various sublimates at different volcanoes [Houtermans *et al.*, 1964; Le Guern, 1988], and notably at Merapi [Le Guern and Bernard, 1982; Symonds *et al.*, 1987; Kavalieris, 1994]. ^{210}Pb behaves chemically as stable lead and is involved in such Pb-

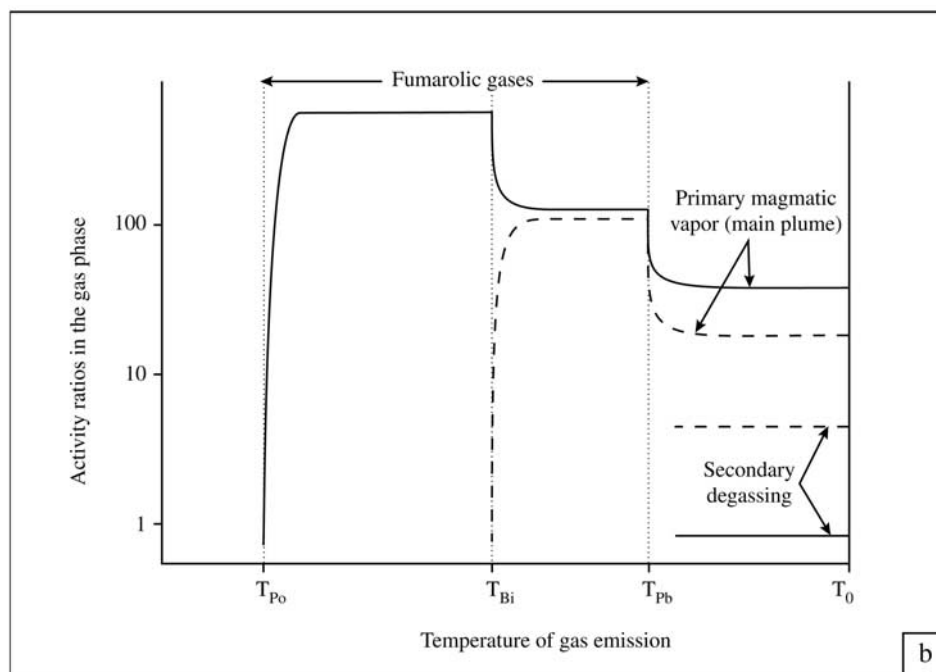


Figure 5b. Theoretical evolution of ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios (dashed line) and ($^{210}\text{Po}/^{210}\text{Pb}$) activity ratios (solid line) in the gas phase as a function of the temperature of gas emission (arbitrary scales on both axes; T_X represents the temperature of condensation of X). Primary magmatic vapor released at a temperature close to that of the magma (T_0) is characterized by high activity ratios that are directly constrained by the respective volatilities of the three nuclides, that is ($^{210}\text{Po}/^{210}\text{Pb}$) > ($^{210}\text{Bi}/^{210}\text{Pb}$). On the other hand, secondary vapor released at high temperature from a previously degassed magma is strongly depleted in the most volatile elements and is characterized by low activity ratios, with ($^{210}\text{Bi}/^{210}\text{Pb}$) > ($^{210}\text{Po}/^{210}\text{Pb}$). In fumarolic gases emitted at temperatures below T_{Pb} , ^{210}Pb is held in sublimates, where it decays into ^{210}Bi . Activity ratios in fumarolic gases, which are thus depleted in ^{210}Pb , mostly depend on the behavior of ^{210}Bi within the sublimates. As long as $T > T_{\text{Bi}}$, ^{210}Bi ingrowth atoms are degassed, and gases are characterized by very high ($^{210}\text{Po}/^{210}\text{Pb}$) and ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios. When $T < T_{\text{Bi}}$, ^{210}Bi is also retained in Pb-sublimates and decays into ^{210}Po , which is in turn degassed for temperatures above T_{Po} . Such gases have very high ($^{210}\text{Po}/^{210}\text{Pb}$) and very low ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios.

sublimates. However, it decays in the sublimates following the radioactivity laws, giving rise to a new ^{210}Bi flux which is emitted as long as the temperature is high enough, or else which decays itself into ^{210}Po [Le Cloarec *et al.*, 1994]. The presence of such Pb-sublimates cannot be ruled out within the dome fractures, where gases circulate and interact with host rocks before reaching the atmosphere. The temperature is high enough to ensure that ^{210}Bi issued from the decay of sublimated ^{210}Pb is volatilized and transported with the main magmatic component. Short-scale temperature variations might thus explain the variability of the ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios measured in the main plume.

[14] Noteworthy is also the fact that samples collected in the main plume are SO_2 -rich, which emphasizes their primary magmatic origin. Although there is little scattering of our data, which might be explained by heterogeneities in the plume chemistry from one degassing vent to another, the overall positive correlations between radionuclide activities and SO_2 concentrations (Figure 6), suggest a common magmatic origin for all these components, and allow one to calculate averaged (^{210}Po)/ SO_2 and (^{210}Pb)/ SO_2 ratios in the main plume in 1995 at $17 \pm 2 \text{ Bq g}^{-1}$ ($R^2 = 0.57$) and

$0.32 \pm 0.04 \text{ Bq g}^{-1}$ ($R^2 = 0.41$), respectively. Accordingly, we propose that samples collected in the main plume represent the most primary magmatic gas, probably directly tapped from the shallow degassing reservoir by the major fissures within the 1961 crater.

3.3. Fumarolic Gases

3.3.1. Gendol

[15] Temperature of gases at Gendol was high all the time, between 650 and 830°C, slightly lower than the magma temperature which is about 900°C at the surface of the degassing reservoir [Le Guern *et al.*, 1982; Bernard, 1985]. This observation is clearly related to the magmatic origin of gases sampled at Gendol, which is also confirmed by the high SO_2 content in the samples. Nevertheless, ($^{210}\text{Po}/^{210}\text{Pb}$) activity ratios vary in a large range, from about 40 in 1990 and 1993, to about 200 in 1988. ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios also vary between 100 and 200 during the same period, except in 1995 when these ratios were as low as 16 on average. Furthermore, both (^{210}Po)/ SO_2 and (^{210}Pb)/ SO_2 ratios vary throughout the study period by one order of magnitude.

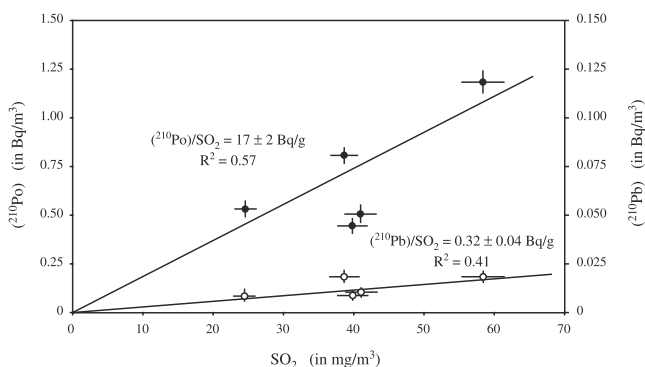


Figure 6. Plot of (^{210}Po) activity (solid symbols) and (^{210}Pb) activity (open symbols) versus SO_2 concentration in gas samples collected in the main plume in 1995. Error bars, given at the 1σ confidence level, are based on analytical uncertainties.

[16] All of this strongly suggests that the gaseous phase includes another component besides the magmatic one. As mentioned above, sublimates are an effective source of ^{210}Bi and ^{210}Po , by the way of ^{210}Pb condensation before the output of the gases in the atmosphere. Pb sublimates are deposited precisely in the range of temperatures prevailing in the ground at Gendol [Bernard, 1985; Symonds *et al.*, 1987; Kavalieris, 1994]. ^{210}Bi and ^{210}Po are thus produced by radioactive decay of ^{210}Pb in the sublimates and subsequently released in the magmatic gas phase according to the volatility of their salts. Therefore the variability of both ($^{210}\text{Po}/^{210}\text{Pb}$) and ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios might be tentatively linked to the temperature of gas emissions (Figure 5b).

[17] From 1979 to 1988, fumaroles temperature was all the time close to 800°C . At such a temperature, it is likely that ^{210}Bi is only partly degassed from the sublimates. Remaining ^{210}Bi atoms thus decay into ^{210}Po atoms that are in turn completely degassed. This would explain why both ($^{210}\text{Po}/^{210}\text{Pb}$) and ($^{210}\text{Bi}/^{210}\text{Pb}$) activity ratios had high values at that time. On the other hand, the temperature of the fumaroles at the time of sampling in 1995 was slightly lower (around 650°C on average), possibly preventing ^{210}Bi from being degassed from the sublimates. This would favor a higher production of ^{210}Po atoms by radioactive decay and their subsequent emission in the gas phase, leading to high ($^{210}\text{Po}/^{210}\text{Pb}$) ratios and low ($^{210}\text{Bi}/^{210}\text{Pb}$) ratios. Conversely, activity ratios measured from 1990 to 1993 might be explained by an increase in the fumaroles temperature, leading to the complete volatilization of ^{210}Bi and a drastic decrease in ^{210}Po ingrowth in the sublimates. However, the lack of temperature measurements at that time makes this hypothesis impossible to prove. Alternatively, the low ($^{210}\text{Po}/^{210}\text{Pb}$) activity ratios measured in August 1990, at the time of a strong degassing event likely related to the injection of deep magma (Figure 2), resemble those measured in the main plume and could also represent the signature of a primary magmatic puff.

3.3.2. Woro

[18] Fumarolic gases at Woro were always sampled at about 600°C , except in 1979 when the collection was also performed at 220°C . It can be seen immediately that 1979

samples, collected at both 220°C and 650°C , are characterized by higher activity ratios and much higher radionuclide activities than the other samples. It is worth noting that these samples were collected at the extremity of a silica tube introduced into the fumarolic vent, as described by *Le Guern and Bernard* [1982]. High activities are thus explained by a lower dilution of the gas, while high activity ratios reflect a strong depletion in ^{210}Pb due to lead deposition on the inner walls of the tube, as temperature decreases. Because of this artifact that fractionates the three radionuclides, 1979 samples are not representative of gas discharges at Woro and they will not be discussed any further.

[19] Regarding the other samples, the (^{210}Po) versus (^{210}Pb) dilution line is shown in Figure 7. The ($^{210}\text{Po}/^{210}\text{Pb}$) ratio remained constant for the whole study period and is equal to 51 ± 3 ($R^2 = 0.95$), very close to the ratio measured in the main plume. This suggests that both ^{210}Po and ^{210}Pb have a unique magmatic origin, which is also consistent with the correlations between (^{210}Po), (^{210}Pb), and SO_2 observed in 1994–95 (Figure 8). However, at least three questions arise from this unexpected situation. One is the apparent lack of contribution from sublimates in fumaroles of lower temperatures, while such sublimates are obviously present at Woro [e.g., Symonds *et al.*, 1987]; the second is

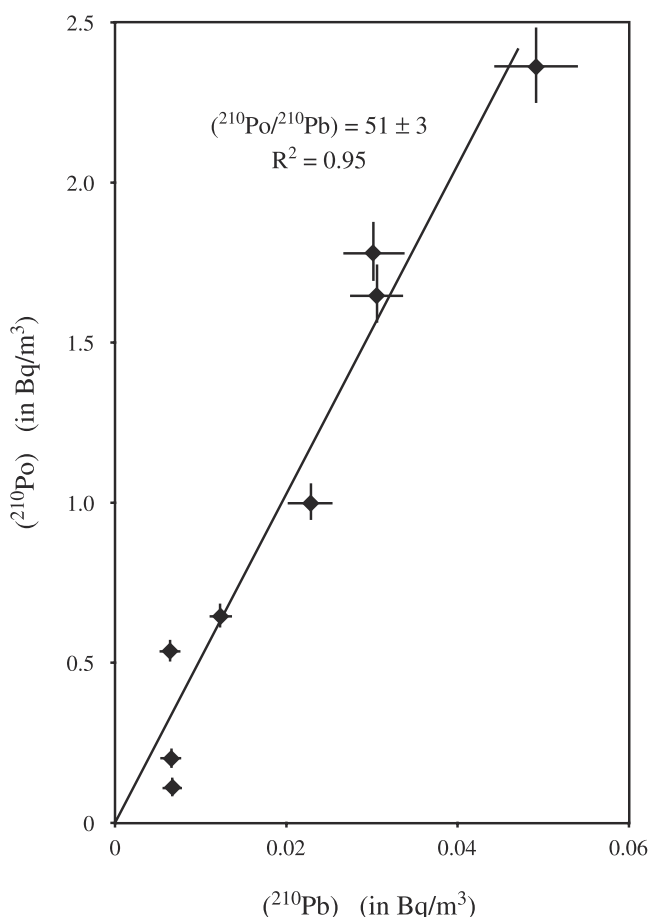


Figure 7. Plot of (^{210}Po) activity versus (^{210}Pb) activity in gas samples collected at Woro, but 1979 samples (see text for explanation). Error bars (1σ) are based on counting statistics.

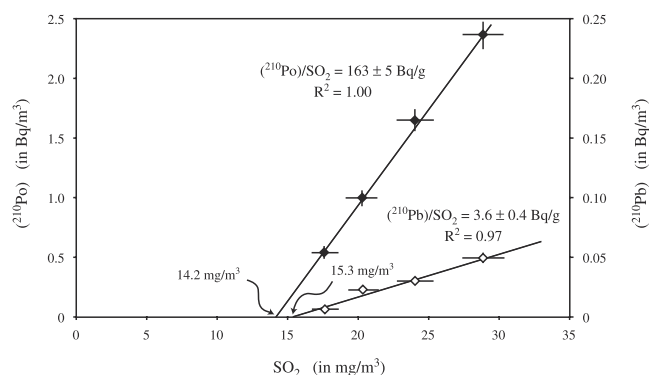


Figure 8. Plot of ^{210}Po activity (solid symbols) and ^{210}Pb activity (open symbols) versus SO_2 concentration in gas samples collected at Woro in 1994–95. Error bars, given at the 1σ confidence level, are based on analytical uncertainties.

the presence of an excess of SO_2 (about 15 mg m^{-3} of air) in gas samples collected at Woro; and finally, one can wonder why the $^{210}\text{Po}/\text{SO}_2$ and $^{210}\text{Pb}/\text{SO}_2$ ratios are one order of magnitude higher than in the main plume.

[20] As already explained for ^{210}Po vs. ^{210}Pb plots, linear correlations in Figure 8 represent the dilution of the volcanic gas (i.e., magmatic component plus sublimate-derived component) by the ambient air at the point of sampling. As a standard continental atmosphere contains negligible amounts of SO_2 and radionuclides, such dilution lines should intercept at 0, 0. This is obviously not the case at Woro, where the local atmosphere contains an excess of SO_2 of about 15 mg m^{-3} of air. This can be achieved only by assuming that it results from the diffuse degassing of SO_2 through the soil in this area, where it mixes with the air flux circulating inside the volcano.

[21] The very high $^{210}\text{Po}/\text{SO}_2$ and $^{210}\text{Pb}/\text{SO}_2$ ratios could either result from the contribution of a non-primary magmatic source of ^{210}Po and ^{210}Pb and/or from the lowering of the magmatic SO_2 . At 600°C , sublimates deposited in this area are a possible source of ^{210}Po , as indicated above. However, they do not explain the high ^{210}Pb component, so that this first hypothesis has to be ruled out, hence pointing out that SO_2 is actually depleted in gases sampled at Woro.

[22] All the above observations can be explained if we make the assumption, in reference to Giggenbach's studies at White Island, New Zealand [Giggenbach, 1987], that the gas chemistry at Woro is controlled by the presence of brines buffering magmatic gases before their emission. It is worth noting that the Woro fumarolic field is located on the edge of the former 1931 crater, now partly filled with eruptive products. This topographic limit might well favor the development of a water-saturated level as suggested by self-potential measurements [Aubert et al., 2000]. If this assumption is correct, magmatic gas would thus dissolve into the brines, whose temperature governs the $\text{SO}_2\text{-H}_2\text{S-H}_2\text{O}$ equilibrium [Giggenbach, 1987]. This would best explain not only the SO_2 -depletion in gases collected at Woro (by the way of the transformation of magmatic SO_2 into H_2S), but also the origin of the diffuse degassing of SO_2 (by the way of the homogenization of SO_2 within the

brines, prior to its degassing beneath the entire fumarolic area). In the same way, radionuclides are likely to condense when entering the brines, and are subsequently degassed according to the emanation coefficient of their volatile compounds at a nearly constant temperature of 600°C . Accordingly, activity ratios as well as both $^{210}\text{Po}/\text{SO}_2$ and $^{210}\text{Pb}/\text{SO}_2$ ratios are characteristic of the brines, which explains the apparent steady-state $^{210}\text{Po}/^{210}\text{Pb}$ ratio in the samples. On the other hand, as for samples collected at Gendol, $^{210}\text{Bi}/^{210}\text{Pb}$ activity ratios display extreme variations, which suggests that, besides the brines control, sublimates may also account for the isotopic signature of gas emanations at Woro.

3.4. Summary

[23] This complete survey of ^{210}Po - ^{210}Bi - ^{210}Pb short-lived radioactive disequilibria in volcanic gases at Merapi Volcano, Indonesia, shows that radionuclide contents in gases emitted from the summit area are characteristic of the degassing processes and gas paths within the edifice. Gases released at both Gendol and Woro fumarolic fields are clearly of magmatic origin, as evidenced by their high temperatures and SO_2 contents. However, as far as U-series isotopes are concerned, their magmatic signature is strongly altered by secondary processes such as condensation and transformation of gases when crossing brines (Woro), and deposition of Pb-sublimates followed by subsequent degassing of radioactive decay products according to temperature variations in the ground (Woro, Gendol). High-temperature gases collected in the main plume, released through large fractures within the 1961 summit crater, are characterized by high SO_2 contents, as well as radioactive disequilibria which are directly constrained by the respective volatilities of the isotopes. These features are related to the magmatic origin of the gas phase which is directly tapped in the degassing reservoir or conduit, and which escapes through the main fractures with little interaction with the dome-forming host rocks. Accordingly, gas samples collected in the main plume represent the most primary magmatic gases available at Merapi Volcano and they are the only ones suitable to derive information on shallow magmatic processes, as shown below. Finally, gases arising from the growing dome are strongly depleted in the most volatile isotopes or compounds. They likely result from the secondary, crystallization-driven degassing of a magma batch that previously lost its volatiles in the shallow reservoir or in the conduit to supply gases to the main plume and the two fumarolic fields.

[24] These results show that magmatic degassing at Merapi Volcano is an open-system process during which volatiles escape easily from the magma during its ascent toward the surface, probably by shear-induced deformation of gas vesicles that allows rapid transfer of volatiles to the periphery of the magmatic conduit [Le Pennec et al., 2001]. Open-system degassing implies that gases do not accumulate at depth and hence that any overpressure in the magmatic conduit or reservoir cannot be due to gas buildup. This explains why present-day Merapi eruptions usually display no, or only little, explosive component, but instead mostly consist in gravitational dome-collapse events to produce the so-called "Merapi-type" block-and-ash flows [Voight et al., 2000]. Furthermore, the fact

that lava domes are almost completely degassed at the time of their emplacement can explain why pyroclastic surges, generated by fragmentation of gas-pressurized dome clasts within the block-and-ash flows, are not systematically observed during dome-collapse events at Merapi [Kelfoun, 1999], contrary to what happens on other andesitic arc-volcanoes, like Soufrière Hills, Monserrat [Sparks and Young, 2002].

4. Radionuclide Degassing From Andesitic Magmas

4.1. Radionuclide Volatility in Volcanic Gases

[25] Metal volatility is often described in the literature by use of an enrichment factor (EF), based upon the relative concentrations of a trace element in both the gas phase and the lava, which are normalized to the same concentrations for a reference element. According to this definition, enrichment factors cannot account for the intrinsic volatility of a trace element, since they mostly depend on the choice of the normalizing element. For this reason, emanation coefficients (ϵ) are more widely used. They are defined as the ratio of the number of atoms of any stable volatile trace element (X) released in the gaseous phase (N_G^X) to the number of atoms initially present in the undegassed magma (N_0^X): $\epsilon_X = N_G^X/N_0^X$ [Lambert *et al.*, 1985]. Owing to this definition, emanation coefficients range from 0% for non-volatile elements, to 100% for gases and highly volatile elements, like Po in basaltic systems [Lambert *et al.*, 1985]. Emanation coefficients of ^{210}Pb , ^{210}Bi , and ^{210}Po have been either directly measured at various volcanoes or recalculated from published EF [Rubin, 1997]. For instance, the emanation coefficient of lead was measured at 1.5% at Stromboli Volcano, where magma temperature is close to 1050°C [Gauthier *et al.*, 2000], and at 1% at Mount Etna for a magma temperature of about 1000°C [Pennisi *et al.*, 1988; Gauthier and Le Cloarec, 1998]. The same authors found that ϵ_{Bi} is in the range 14–24% at Stromboli, and 8–22% in Mount Etna's plume. These estimates of both lead and bismuth volatilities are in good agreement with average mafic emanation coefficients compiled by Rubin [1997]. Finally, the emanation coefficient of ^{210}Po is very high in hot basaltic systems (100% at both Mount Etna [Le Cloarec *et al.*, 1984] and Kilauea [Gill *et al.*, 1985]), while it is slightly lower (85%) in the 1075°C basic andesite from Arenal [Gill *et al.*, 1985]. It thus appears that emanation coefficients are closely related to the temperature of the magma and to its composition. Besides this, emanation coefficients also depend on the composition of the gas phase, namely on the respective proportions of the different volatile species involved in metal transportation in volcanic gases, for instance presence or lack of fluorides [Gauthier *et al.*, 2000].

4.2. Emanation Coefficients of Pb, Bi, and Po at Merapi

[26] Previous works on Mt. Etna and Stromboli Volcanoes suggest that the escape time of gas bubbles from a degassing magma batch (i.e., the time that elapses between bubble nucleation in the magma reservoir and gas emission in the atmosphere) usually does not exceed a few hours to a few days at most [Lambert *et al.*, 1985;

Table 2. Stable Lead and Bismuth Concentrations in Merapi Lavas and Associated Gases

	Lava, mg g ⁻¹	DMP3, ^a mg m ⁻³	DMP4, ^a mg m ⁻³
Bi	0.43 ± 0.13 ^b	0.33	0.26
Pb	18.0 ± 1.2 ^c	4.33	2.42

^aPb and Bi measured by ICP-MS (A. Gaudry, analyst).

^bBi measured by AAS using hydride technique. Mean value for lava samples erupted between 1978 and 1993 [Nho *et al.*, 1996].

^cPb measured by ID-ICP-MS. Mean value for lava samples erupted between 1984 and 1995 [Gauthier and Condomines, 1999].

Gauthier *et al.*, 2000]. While these studies regard basaltic systems, it can be assumed that gases at Merapi also reach the surface shortly after bubble nucleation since ^{210}Bi - ^{210}Pb disequilibria are well preserved in Merapi gases ($t_{1/2}^{210}\text{Bi} = 5$ days). Because ^{210}Pb half-life ($t_{1/2} = 22.3$ yr) is much longer than degassing timescales, radioactive decay of this isotope within gas bubbles is negligible. It is thus possible to estimate ϵ_{Pb} using the (^{210}Pb)/ SO_2 ratio in the main plume. Taking into account the definition of ϵ , this ratio is equal to $\epsilon_{\text{Pb}} * (^{210}\text{Pb})_0 / \epsilon_{\text{SO}_2} * [\text{SO}_2]_0$, where $(^{210}\text{Pb})_0$ and $[\text{SO}_2]_0$ represent the (^{210}Pb) activity and the SO_2 concentration, respectively, in the magma before degassing. Study of melt inclusions and residual glasses shows that $[\text{S}]_0 = 0.9$ mg g⁻¹ and $\epsilon_{\text{S}} = 90\%$ (N. Métrich, personal communication, 1999). Although both SO_2 and H_2S species may coexist in Merapi gases [Le Guern *et al.*, 1982], it is reasonable to assume that all the H_2S is oxidized into SO_2 at the time of sampling of the diluted plume on filters, so that we have $[\text{SO}_2]_0 = 1.8$ mg g⁻¹ and $\epsilon_{\text{SO}_2} = 90\%$. From $(^{210}\text{Pb})_0 = 0.055 \pm 0.001$ Bq g⁻¹ (averaged value of (^{226}Ra) activity in 8 lava samples, assuming ^{226}Ra - ^{210}Pb equilibrium in the undegassed magma and taking into account the effect of degassing (concentration of non volatile elements in the liquid phase) on (^{226}Ra) activities in lavas [Gauthier and Condomines, 1999]) and $(^{210}\text{Pb})/\text{SO}_2 = 0.32$ Bq g⁻¹ (this work), it comes $\epsilon_{\text{Pb}} = 0.94 \pm 0.15\%$, not very different from the values quoted above for basaltic systems.

[27] The emanation coefficient of any stable volatile trace element X can be inferred from the value of ϵ_{Pb} and concentration measurements in both aerosols (G) and lavas (L), according to the following mass conservation equation [Lambert *et al.*, 1985]:

$$\epsilon_X = \left[1 + \frac{1 - \epsilon_{\text{Pb}}}{\epsilon_{\text{Pb}}} \times \frac{[\text{Pb}]_G}{[\text{Pb}]_L} \times \frac{[\text{X}]_L}{[\text{X}]_G} \right]^{-1}. \quad (1)$$

[28] Regarding bismuth, the very short half-life of ^{210}Bi (5 days) requires to use the stable isotope ^{209}Bi to calculate ϵ_{Bi} . From $\epsilon_{\text{Pb}} = 0.94\%$, and both Bi and Pb measurements in 1995 aerosol samples and in selected 1978–1995 lava samples (Table 2), we calculate with equation (1) a mean value for ϵ_{Bi} of $3.5 \pm 0.7\%$, which is very low compared to those observed at Etna and Stromboli. Using published data on Bi and Pb concentrations in sublimates, incrustations and condensates from both Woro and Gendol fumarolic fields [Symonds *et al.*, 1987] leads to a still lower value ($\epsilon_{\text{Bi}} = 0.5\%$), which emphasizes the large influence of temperature on bismuth volatility.

Table 3. Melting Temperature (T_m), Boiling Temperature (T_b), Partial Pressures (Pp), and Emanation Coefficients (ϵ) of the Main Volatile Compounds of Pb, Bi, and Po^a

Compound	T_m , °C	T_b , °C	Pp Within Range of Magmatic Temperatures T_0 , °C ^b					ϵ , % Within Range of Magmatic Temperatures T_0 , °C ^c				
			1050	1000	950	900	850	1050	1000	950	900	850
PbF ₂	830	1293	0.093	0.053	0.030	0.016	0.008	1.5	0.86	0.48	0.26	0.13
PbCl ₂	501	951	gas	gas	1	0.609	0.302	1.5	1.5	1.5	0.91	0.45
PbBr ₂	371	892	gas	gas	gas	1	0.631	1.5	1.5	1.5	1.5	0.95
PbS	1118	ND	0.0439	0.0188	0.0077	0.0030	0.0011	1.5	0.64	0.26	0.10	0.04
Pb	327	1749	0.0024	0.0013	0.0007	0.0003	0.0002	1.5	0.81	0.44	0.19	0.12
BiF ₃	725	900	gas	gas	gas	1	ND	20	20	20	20	ND
BiCl ₃	230	447	gas	gas	gas	gas	gas	20	20	20	20	20
BiBr ₃	218	453	gas	gas	gas	gas	gas	20	20	20	20	20
Bi ₂ S ₃	850	ND	ND	ND	ND	ND	ND	20	ND	ND	ND	ND
Bi	271	1564	0.0069	0.0035	0.0018	0.0008	0.0004	20	10.3	5.1	2.5	1.1
PoCl ₄	300	390	gas	gas	gas	gas	gas	100	100	100	100	100
Po	254	962	gas	gas	0.928	0.575	0.347	100	100	93	57	35

^aData from Lide [1997]. ND is no data available.^bPartial pressures at 0.1 MPa [Lide, 1997].^cTheoretical emanation coefficients are calculated from measured emanation coefficients in hot basaltic systems, assuming that each element is degassed as a single species (see text).

[29] The case of ²¹⁰Po is more complicated since no stable isotope can be used in place of this short-lived isotope ($t_{1/2} = 138$ days). Accordingly, the best and most accurate way to determine a ²¹⁰Po emanation coefficient usually is to measure its activity and monitor its radioactive ingrowth in freshly erupted lava samples of accurately known eruption dates [e.g., Gill *et al.*, 1985]. However, this cannot be achieved at Merapi where collection of such lava samples is feasible only during periods of high effusive activity right after dome-collapse events, which is of obvious hazard and was never performed until now. It is worth mentioning that the collection of a frozen lava dome sample during quieter periods of activity cannot be envisaged either. Indeed, it is most of the time impossible to determine whether such a sample has been erupted days, weeks, or even months before its collection, making it impossible to determine accurately the initial ²¹⁰Po activity upon eruption and hence the ²¹⁰Po emanation coefficient. Nevertheless, it is still possible to approximate to the value of ϵ_{Po} by using the (²¹⁰Po/²¹⁰Pb) activity ratio measured in the main plume where the most primary magmatic vapor is released (see section 3.2). As explained above, the escape time of gases probably does not exceed a few days at Merapi, since disequilibria between ²¹⁰Pb and the very short-lived ²¹⁰Bi are preserved in the gas phase. It means that ²¹⁰Po decay within gas bubbles can be neglected. (²¹⁰Po/²¹⁰Pb) activity ratios measured in the main plume are thus very close to their value at the time of gas exsolution in the degassing reservoir. For very short magma residence times compared to ²¹⁰Po half-life, this value is merely equal to $\epsilon_{Po}/\epsilon_{Pb}$ [Gauthier *et al.*, 2000]. From (²¹⁰Po/²¹⁰Pb) = 56 and $\epsilon_{Pb} = 0.94\%$, it would thus come $\epsilon_{Po} = 53 \pm 9\%$. Unfortunately, this condition is not valid at Merapi, where previous work on ²¹⁰Pb-²²⁶Ra disequilibria in lavas showed that magma residence time in 1995 was close to 2 years [Gauthier and Condomines, 1999]. Owing to the exact definition of the emanation coefficient for a radioactive isotope [see Gauthier *et al.*, 2000, Appendix], it can be easily demonstrated that emanation coefficients of short-lived radionuclides decrease for increasing values of the magma residence time. Our estimate of ϵ_{Po} must thus

be regarded as an upper limit. Whatever the exact value of $\epsilon_{Po} \leq 53\%$, this new result is considerably lower than those previously reported for basaltic systems.

4.3. Volatile Species Involved in Radionuclide Degassing

[30] The comparison of the emanation coefficients determined at Merapi with usual values measured in higher-temperature basaltic systems provides a basis to estimate volatile species involved in the degassing of radionuclides. Indeed, data given in Table 3 suggest that some volatile radionuclide compounds can be affected by the lower temperature of Merapi's andesites (900°C), thus resulting in lower emanation coefficients.

[31] Among volatile Pb compounds, the one that shows the smallest partial pressure variations within the range of magmatic temperatures is PbCl₂, whose boiling point is at 951°C (Table 3). A simple calculation, based on the assumption that lead is released in the gas phase as a single volatile compound, shows that the variations of PbCl₂ partial pressures yield a decrease in ϵ_{Pb} from 1.5% at 1050°C down to 0.91% at 900°C, which is in excellent agreement with the measured value at Merapi (Table 3). The same calculation for Pb-fluoride, -sulfide, and -metal gives much lower results at 900°C, in the range 0.10–0.26%. Finally, values of ϵ_{Pb} derived from PbBr₂ data remain constant at all magmatic temperatures above 900 °C. Although thermodynamical modeling of gas emissions at both St. Helens and Etna Volcanoes suggests that halogenide, sulfide, and metal compounds may coexist in the gas phase at high temperature [Le Guern, 1988], these new results show that Pb is predominantly degassed as a chloride. In addition, bromide may also be involved in the transportation of Pb in volcanic gases, in good agreement with previous observations on South American volcanoes [Gemmell, 1987].

[32] Since all bismuth halogenides are gaseous at low temperatures (Table 3), emanation coefficients should not vary within the range of magmatic temperatures if bismuth was degassed as such compounds. On the other hand, observed variations of ϵ_{Bi} are consistent with its emission

as a metal, or perhaps as a sulfide (no data available), as predicted by thermodynamical modeling [Le Guern, 1988].

[33] Finally, the decrease in ^{210}Po volatility in lower-temperature gas emissions from Merapi cannot be accounted for by its degassing as PoCl_4 , whose boiling point is very low (390°C). It can be concluded that polonium is mostly transported in volcanic gases as a metal since the predicted value of ε_{Po} at 900°C (57%) is in very good agreement with our actual estimate ($\leq 53 \pm 9\%$).

5. Volume of the Degassing Reservoir

[34] The SO_2 flux emitted in the main plume was regularly measured by COSPEC from 1987 to 1995 [Nho *et al.*, 1996; Smithsonian Institution, 1994, 1995], leading to an average value of $90 \pm 20 \text{ Mg d}^{-1}$. The ^{210}Pb flux is easily inferred from this flux and from the $(^{210}\text{Pb})/\text{SO}_2$ ratio measured in the main plume in 1995 (this work), that is $\phi_{210\text{Pb}} = 29 \pm 7 \text{ MBq d}^{-1}$. This flux is sustained by a daily input ϕ_0 into the degassing reservoir of deep undegassed magma whose ^{210}Pb activity is about $(^{210}\text{Pb})_0 = 0.055 \text{ Bq g}^{-1}$, emitted at a rate of $\varepsilon_{\text{Pb}} = 0.94\%$. We thus have $\phi_0 = \phi_{210\text{Pb}} / ((^{210}\text{Pb})_0 * \varepsilon_{\text{Pb}}) = 5.6 \pm 1.7 * 10^{10} \text{ g d}^{-1}$, or else $\phi_0 = 690,000 \pm 210,000 \text{ m}^3 \text{ month}^{-1}$ using a magma density of $2,500 \text{ kg m}^{-3}$. Using the average residence time (τ) of 2 years determined for the post-1992 period by Gauthier and Condomines [1999], it is now possible to estimate the volume of the shallow degassing reservoir, which is merely given by $V = \phi_0 * \tau$. It comes $V = 1.7 \pm 0.5 * 10^7 \text{ m}^3$, in very good agreement with the volume inferred by these authors from the lava extrusion rate at the surface in 1992.

[35] On the basis of seismological studies, a magma chamber has been postulated at 1.5 km depth below the summit, with a volume of 2.6 km^3 [Ratdomopurbo, 1995]. The feeding conduit between the roof of the chamber and the summit crater has a volume of about $3 * 10^6 \text{ m}^3$, assuming it has a cylindrical shape and a diameter of 50 m [Siswowidjoyo *et al.*, 1995; Le Pennec *et al.*, 2001]. This is about one order of magnitude smaller than the volume of the degassing reservoir calculated here, so that we can conclude that degassing mostly occurs in the shallow magma chamber.

6. Shallow Magma Dynamics and Implications for Eruptive Activity at Merapi

[36] From the estimate of the volume of degassing magma calculated above, the influx of deep magma ϕ_0 brought into the degassing reservoir can be determined for the poorly active 1984–92 eruptive cycle. During this cycle, a minimum magma residence time of 22 years has been estimated on the basis of ^{226}Ra – ^{210}Pb disequilibria in lavas [Gauthier and Condomines, 1999; Condomines *et al.*, 2003]. This yields an input of deep magma ϕ_0 of about $65,000 \text{ m}^3 \text{ month}^{-1}$, that is 1.6 times the average eruption rate for this period ($40,000 \text{ m}^3 \text{ month}^{-1}$; Figure 2). Noteworthy, the deep undegassed magma input ϕ_0 brought into the degassing reservoir in 1995 ($690,000 \text{ m}^3 \text{ month}^{-1}$) is also 2.3 higher than the average lava output erupted during the eruptive cycle that began in 1992 ($300,000 \text{ m}^3 \text{ month}^{-1}$; Figure 2). Effusive activity at Merapi thus appears to be

directly related to shallow magma dynamics, each eruptive cycle corresponding to a change in the feeding rate of the magma chamber.

[37] On average, half of the magma brought into the degassing reservoir at Merapi is thus erupted and contributes to the growth of the lava dome. This compares with less than a few per cent at Stromboli Volcano [Allard *et al.*, 1994; Gauthier *et al.*, 2000], as well as many other persistently degassing volcanoes [Andres *et al.*, 1991]. Although degassing-driven convection has proved efficient in andesitic magmas [Kazahaya *et al.*, 1994], yet this observation might be related to the different rheologies of both magmas at Stromboli and Merapi. Sinking of the degassed magma into the ascending undegassed magma might be indeed more difficult in the more viscous andesitic magma of Merapi.

[38] Long-term averaged effusive rate of lava at Merapi has been estimated at about $10^5 \text{ m}^3 \text{ month}^{-1}$ [Siswowidjoyo *et al.*, 1995]. Assuming that the ratio between the deep magma input and the lava output at the surface remained constant over the last two centuries of almost continuous activity at Merapi, 0.24 km^3 of degassed magma would thus have been unerupted, that is recycled and stored at depth. This volume must be regarded as a maximum estimate insofar as eruptive rates are based on the volume of the growing domes, hence neglecting the volume of rocks falling from the domes during the so-called guguran (rock-falls in Indonesian) episodes. As a consequence, the ratio intrusive/extrusive magma might be slightly lower than 1. No matter the exact volume of unerupted degassed magma at Merapi, this model implies that the shallow magma chamber would have significantly inflated (by about 10%) over the two last centuries. With respect to actual deformation measurements recorded at Merapi [Beauducel and Cornet, 1999], this seems quite unlikely.

[39] We thus propose another scenario for magma dynamics beneath Merapi, based on observed variations of the lava dome extrusion rate during the 1992–95 eruptive cycle. It can be seen in Figure 2 that extrusion rates at the beginning of each phase of dome growth (February 1992, February 1994, and November 1994) are always very high, up to $0.7 * 10^6 \text{ m}^3 \text{ month}^{-1}$ in 1992 [Siswowidjoyo *et al.*, 1995; Kelfoun, 1999]. Note this is actually equal to the magma input ϕ_0 into the reservoir. Then, lava production regularly decreases, and even almost stops, until a new lobe of lava emerges. It thus appears that when the volcano behaves as an open conduit, all the degassing magma contributes to the growth of the new dome. Because the dome that emplaces within the crater rapidly cools and becomes more viscous, its growth regularly slows down until the system is completely clogged. Meanwhile, the feeding rate of the reservoir remains the same at depth, so that magma progressively accumulates below the summit. Although magma can display an elastic behavior and be compressible [e.g., Blake, 1981], this certainly yields a build-up of pressure, which ultimately leads to the destabilization of the dome when it exceeds its mechanical resistance. For instance, between February 1994, beginning of the 1994-dome growth, and the dramatic eruption of November 1994, $2.6 * 10^6 \text{ m}^3$ of lava have been erupted while $6.2 * 10^6 \text{ m}^3$ of magma have degassed (assuming ϕ_0 remained constant throughout the eruptive cycle). It implies that $3.6 * 10^6 \text{ m}^3$ of degassed

magma have accumulated in the chamber, leading to an increase of the chamber volume equal to 0.14%. It is worth noting that this estimate is very close to the critical value of $\Delta V/V = 10^{-3}$ proposed by Blake [1981] to trigger an eruption. This model could explain why there was no precursor related to a massive reinjection of deep magma before the 1994 eruption [Gauthier and Condomines, 1999; Ratdomopurbo and Poupinet, 2000; Zlotnicki et al., 2000]. It also explains why the domes usually start growing at a rate close to the feeding rate ϕ_0 . Finally, it implies that, contrary to what happens at other degassing volcanoes, all the degassing magma is erupted at the surface.

7. Conclusion

[40] Short-lived radionuclide measurements (^{210}Po - ^{210}Bi - ^{210}Pb) performed in volcanic gases emitted from various locations (fumarolic fields, inactive and growing domes) at Merapi Volcano allow the characterization of different types of degassing processes and gas paths.

[41] The great stability of gas composition at the Woro fumarolic field ($T \sim 600^\circ\text{C}$) is explained by the presence, between magma and surface, of brines that might be also at the origin of a diffuse flux of SO_2 at that place. The pseudo steady-state observed for radioactive disequilibria could be due to gases transformation when they cross these brines which act as a buffer. At the Gendol fumarolic field, the lack of correlation between radionuclides and SO_2 contents indicates that one or more gaseous components mix with the magmatic one, which is obviously present, as shown by the very high temperature of the gases ($T \sim 800^\circ\text{C}$). Sublimates have been shown to be an efficient source of ^{210}Po and ^{210}Bi in gases which are not directly emitted from the magma to the atmosphere, and are likely the main contributing part in the fumarolic gases at Gendol.

[42] The growing dome is completely degassed when it reaches the surface, as shown by the lack of SO_2 and the very weak activity of ^{210}Po . The low ^{210}Po and ^{210}Bi contents in the gases are mostly issued from the decay of ^{210}Pb which is not totally expelled from the magma, due to its very low volatility. This can be explained by fractional degassing processes, primary degassing occurring at shallow depth either in the upper part of the feeding system or in a shallow chamber located below the summit. These primary magmatic gases are emitted in the main plume, released through large fractures crossing the older domes located within the summit crater. Their isotopic signature confirm the greater volatility of ^{210}Po , compared to ^{210}Bi and even more ^{210}Pb . However, their emanation coefficients ϵ are lower ($\epsilon_{\text{Po}} \leq 53\%$, $\epsilon_{\text{Bi}} = 3.5\%$, and $\epsilon_{\text{Pb}} = 0.94\%$) than those usually found at basaltic volcanoes, particularly those of ^{210}Bi and ^{210}Po . It emphasizes the major role played by temperature on trace metal volatility and it is suggested that lead is mainly transported in volcanic gases as a chloride, while bismuth and polonium are degassed as metals.

[43] Radionuclide fluxes in the gas phase in 1995 allow the determination of the deep undegassed magma supply into the degassing reservoir at $690,000 \text{ m}^3 \text{ month}^{-1}$. The volume of the degassing reservoir is calculated from this estimate at about $1.7 \times 10^7 \text{ m}^3$. The deep magma supply is twice the extrusion rate of lava at the surface. It is proposed that the recycling at depth of the unerupted degassed magma

is made difficult because of magma viscosity. This leads to an accumulation of magma below the summit, and subsequently to the build-up of an overpressure that might ultimately trigger eruptions without any precursor, as the November 22, 1994 catastrophic event.

[44] These results emphasize the interest of radioactive disequilibria measurements in volcanic gases as a promising method to characterize degassing processes as well as to infer shallow-level magma dynamics. Time-series analyses of radioactive disequilibria in volcanic gases might thus be used as a geochemical monitoring tool to apprehend any changes in the magma dynamics at active volcanoes, which appears essential not only for a better understanding of their behavior, but also for any attempt to predict the evolution of their volcanic activity.

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